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A modified blister test to study the adhesion of thin coatings based on local helium ion implantation

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Abstract

A modified blister test has been developed based on helium ion implantation into selected areas of the metal substrate prior to the coating deposition. After a post-deposition thermal annealing, blisters are formed by agglomeration of the implanted gas at the ceramic–metal interface. This method can be used to control the pressure in the blister which eventually may lead to delamination at the periphery of the blister. A microsieve with a regular array of circular holes is used during the implantation to assure the initial blister size. Two different microsieves were employed in this work, with pore diameters of 1.5 and 4.5 μm, respectively. The distance between the centres of neighbour pores is twice the pore diameter. Scanning Electron Microscopy (SEM) and Confocal Scanning Optical Microscopy (CSOM) observations allowed the determination of the blistering parameters such as the radius, the height and the blister volume. From the gas content and these parameters, the work of adhesion or energy release rate can be obtained.

In this work, we present the first results of this blister test applied to W–C:H films and multilayers of Ti and Al deposited by Physical Vapour Deposition on polycrystalline copper substrates. The copper substrates were implanted with 34 keV He^+ ions up to fluences of 3 and 5×10^{16} cm^{-2} before the deposition of the coatings and annealed afterwards in vacuum at temperatures from 773 to 1073 K for 30 min. Delamination of the Ti/Al multilayer coatings was already detected after annealing at 873 K with an energy release rate estimated to be 0.5 J m^{-2} at a typical helium pressure of 10^7 Pa. No delamination but only helium swelling was observed for W–C:H coatings annealed at 1073 K. Results of experiments on uncoated copper samples are also shown in order to explain the mechanism of helium bubble growth and helium release that causes the creation of the blisters.

PACS: 68.35.Gy; 62.20.-x; 61.16.Bg; 85.40.R
Keywords: Adhesion; Ion implantation; Ceramics; Metals

1. Introduction

Coatings on materials have numerous applications, which vary from improvement of wear resistance to embellishment of the surface of objects. In coating technology, considerable attention has been paid to reliable ways of measuring the adhesion of coatings to substrates. One standard test has been the blister test, originally proposed in 1961 by Dannenberg [1], involving the injection of a liquid between a substrate and coating in such a way that the coating is detached in the form of a blister. In 1969, Williams [2] introduced the well-known blister test in which gas pressure was built up by feeding gas through a circular hole at the backside of the substrate. He applied this method to measure the fracture energy of thin coatings on rigid substrates. A constrained blister geometry was introduced by Napolitano et al. [3] to avoid uncontrolled growth of the blister at the liquid or gas pressure. This was

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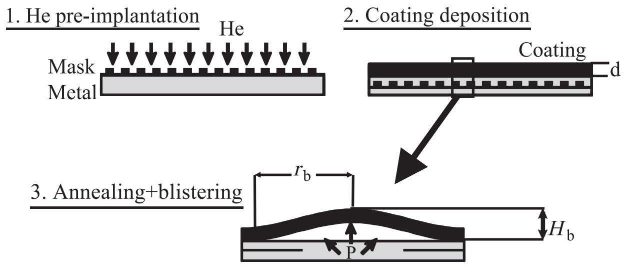

Fig. 1. Schematic representation of the modified blister test proposed. In step 1, the helium ions are implanted in the metal substrate through a mask prior to the coating deposition (step 2). After annealing, the gas is promoted to the interface and causes blistering at the implanted areas by exerting a pressure P to the coating. The radius (r_b) and the height (H_b) of the blisters are related to the adhesion properties of the coatings.

used, among others, by Lai and Dillard [4,5]. The release of gas implanted into the substrate through a polymer film for generating blisters on materials covered with thin films was proposed by Borisenko et al. [6] in 1995. They showed a correlation between gas blister parameters and the adhesion properties of hydrogen-implanted thin silver films on glass substrates. An overview of the theory describing the blister tests is given by Williams [7]. Assuming that the blister lid behaves elastically, the energy release rate (G) in the case of axisymmetric membranes is given by,

$$G = cP_dH_d \quad (1)$$

with c as a geometrical constant ~1, P_d as the pressure and H_d as the height of the blister when delamination occurs.

Against this background, this paper examines the possibility of using gas release from substrates previously implanted with helium to develop an improved blister test to measure the adhesion of the thin coating to the metal substrate. The method aims at improved control over the blister by confining the gas only to a well-defined area. In Fig. 1, the different steps taken during the test are illustrated:

1. Helium ions are implanted in the sample substrate through the holes of a mask;
2. The coating is deposited on the substrate; and
3. By thermal annealing, gas that accumulates at the coating/metal interface is released.

The low permeation of the gas through the coating will lead to the formation of blisters at the interface. The shape and the geometric parameters (height and radius) of the blisters can be measured by means of Confocal Scanning Optical Microscopy (CSOM). They can be used to determine the energy release rate when delamination occurs.

2. Experimental details

In order to test the method, two uncoated polycrystalline copper samples were prepared. Before the implantation, the polycrystalline copper samples were stretched 2% prior to polishing the surface to a roughness lower than 1 μm. Subsequently, they were annealed to remove defects in a vacuum of 10^{-5} Pa at 923 K for 30 min in the presence of hydrogen. The localised gas implantation was performed using a VARIAN 350D ion implanter at 34 keV with fluences of 3 and 3.5×10^{16} He ions/cm^2. The implantations were performed through microsieves with a regular array of pores provided by AquaMarijn Micro Filtration. In Fig. 2, the layout is shown of the copper sample with the location of the microsieve. Two different pore sizes were used for the implantations: 1.5 and 4.5 μm. The distance between the centres of neighbour pores was twice the pore size. As the microsieve partly covered the samples, two implantation zones were considered. These will be referred hereafter as the direct implantation area and microsieve implantation area, respectively (see Fig. 2). The helium implantation depth was 129±57 nm as calculated by TRIM [8]. After the implantation, the samples were heated in a typical vacuum of 10^{-5} Pa to 973 K for 30 min in order to promote the helium ions to surface. Once the copper surface is coated, all this helium will be collected at the interface.

W–C:H films and multilayers of Ti and Al were deposited by Physical Vapour Deposition on polycrystalline copper substrates prepared in a similar way as described above. The W–C:H films were deposited using unbalanced magnetron sputtering in an argon/acetylene atmosphere in a Hauzer HTC-1000 production scale coating system, as described by Strondl et al. in Refs. [9] and [10]. The films have a thickness of 2 μm with an adhesive intermediate chromium layer of 200 nm. The Ti/Al multilayer coatings were deposited at the Universidade de Coimbra (Portugal) from pure Ti and Al targets (99.99%) by d.c. reactive magnetron sputtering. The discharge power applied to Ti and Al targets was 990 and 500 W, respectively, in order to get approximately the same thickness in the individual layers of the coating. The targets with 150×150 mm dimensions were vertically placed at 90° and the substrate holder in the centre of the deposition chamber was rotating. A negative bias voltage of 70 V was applied to the substrate during the deposition and the Ar pressure was 3×10^{-3} Pa. The substrate surfaces were ion-cleaned with an ion gun before coating deposition. The

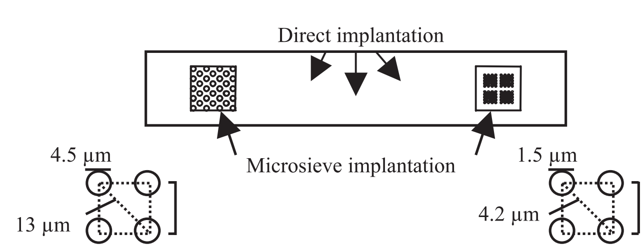

Fig. 2. Top view of the layout of the sample used during implantation. Indicated are the direct and microsieve implantation areas. A closeup of the microsieve areas shows the two different pore sizes (1.5 and 4.5 μm) and periodical array of holes. In the bottom, two confocal pictures show the periodical pattern of the AquaMarijn microsieves with (a) 1.5- and (b) 4.5-μm pore diameters used in the experiments.

cleaning procedure included a first electron heating, up to temperatures close to 450 °C, and afterwards Ar^+ bombardment for 5 min (ion gun settings at 20 A, 40 V, substrates at −70 V). The deposition time was 20 min resulting in a final thickness of 1.6 μm with a periodicity of approximately 20 nm. The coatings were deposited on pre-implanted substrates at 34 keV with fluencies of 3 and 5×10^{16} ions/cm^2. The 4.5-μm pore microsieve was placed on the substrates during the implantation before the Ti/Al multilayers were deposited. The samples were annealed afterwards in vacuum (10^{-5} Pa) during 30 min in steps of 100 K from 773 to 973 K. In the case of W–C:H films, both 1.5- and 4.5-μm pore microsieves were used during pre-implantation and the post-deposition annealing temperatures ranged from 773 to 1073 K. Both types of coatings were also deposited on non-implanted substrates and annealed under the same conditions in order to compare with the pre-implanted samples.

A Philips XL30-S Field Emission Gun Scanning Electron Microscope (FEG SEM) and a μSurf Confocal Scanning Optical Microscope from Nanofocus Meβtechnique were used to observe the coatings and quantify blistering parameters such as the radius and the height. Orientation Imaging Microscopy (OIM) can be also performed in the SEM setup, relating the observed microstructure to corresponding crystal orientations [11].

3. Results and discussion

3.1. Helium implantation on uncoated polycrystalline Cu

In Fig. 3, typical SEM pictures of helium implanted bare copper samples are shown. In Fig. 3a, the periodical pattern of the 4.5-μm microsieve was observed right after the implantation with 2.5×10^{16} ions/cm^2. After annealing at this fluence, see Fig. 3b, the microsieve-implanted areas showed small holes through which gas bubbles have escaped to the surface of the metal. No blisters are observed because in the implanted region, the influence is well below

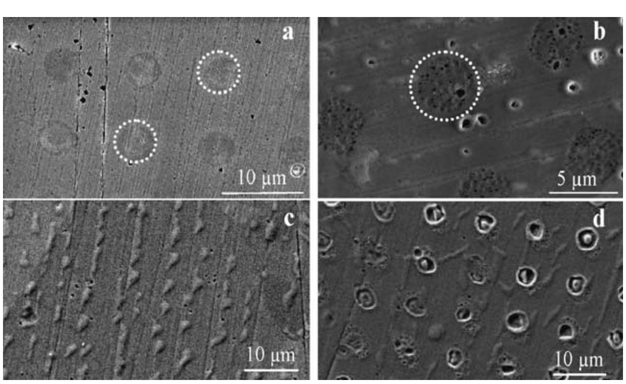

Fig. 3. SEM observation of a polycrystalline copper surface: (a) after helium implantation with 3×10^{16} He ions cm^{-2} through a 4.5-μm microsieve and (b) after subsequent annealing at 973 K. The polycrystalline copper surface after helium implantation at 5×10^{16} cm^{-2} through (c) 1.5- and (d) 4.5-μm microsieves is shown after annealing at 973 K.

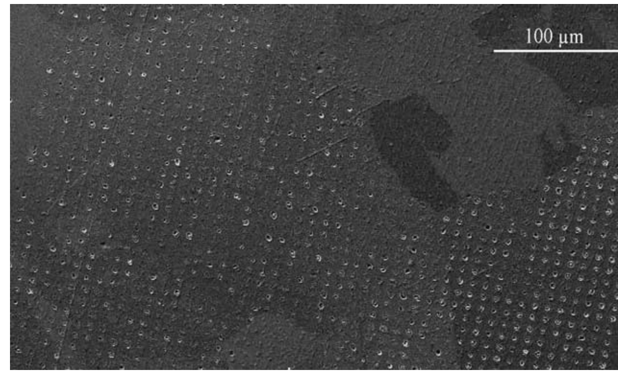

Fig. 4. SEM observation of polycrystalline copper surface after helium implantation at 5×10^{16} He ions cm^{-2} through a 4.5-μm microsieve after annealing at 973 K. The periodical pattern of the microsieve is interrupted at some of the grain boundaries.

the blistering threshold. In Refs. [12] and [13], we gave a detailed description of the mechanism of the helium bubble growth and release mechanisms in the case of helium-implanted copper single crystal. Once a coating is deposited, it is expected that indeed the implanted number of gas atoms can be collected at the interface. Varying the localised gas implantation fluence, different pressures would then be applied to the coatings. In Fig. 3c, it is observed how for an increased fluence of 5×10^{16} ions/cm and a smaller size of pores (1.5 μm), hardly no release holes but instead a periodical blister rows was formed aligned probably along the direction of defects created during polishing. In the case of the 4.5-μm microsieve (see Fig. 3d), the periodical pattern of gas release areas is again observed. In Fig. 4, it is observed that the morphology of gas release areas was remarkably different depending on the grain orientation of

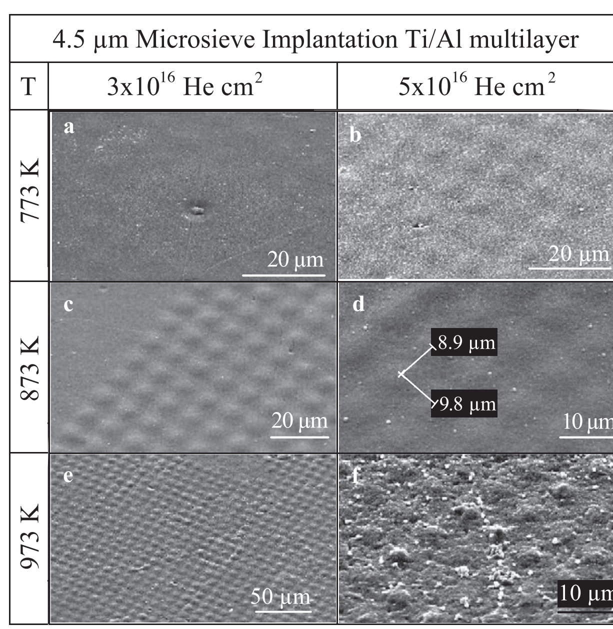

Fig. 5. Selection of SEM pictures in the microsieve area of the surface of the Ti/Al multilayer deposited on polycrystalline copper surface after helium implantation through a 4.5-μm microsieve and annealing.

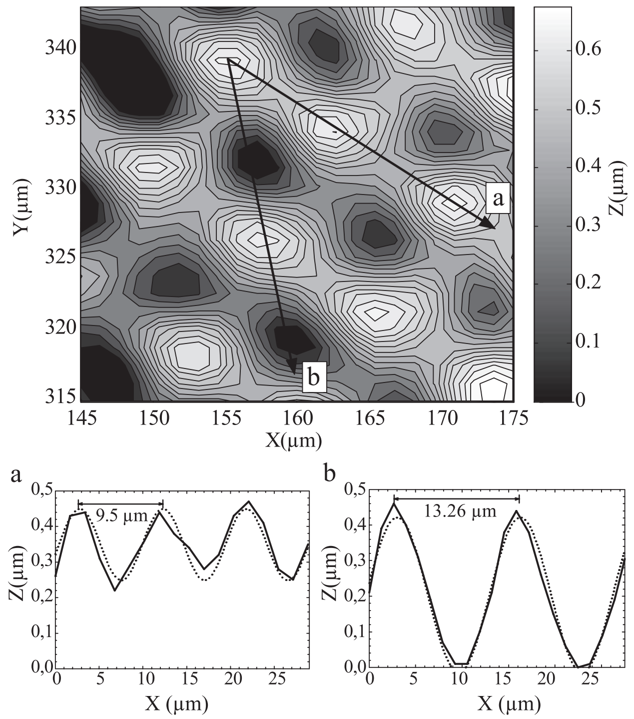

Fig. 6. Contour plot obtained from Confocal Scanning Optical Microscopy (CSOM) measurements performed on the surface of the Ti/Al multilayer deposited on polycrystalline copper surface after helium implantation at 3×10^{16} He ions cm^{-2} through a 4.5-μm microsieve after annealing at 973 K. The periodicity of the blistering pattern is clearly observed. The blisters are interconnected in the direction of the nearest neighbour (a). At the bottom of the figure, profiles taken in directions (a) and (b) are shown.

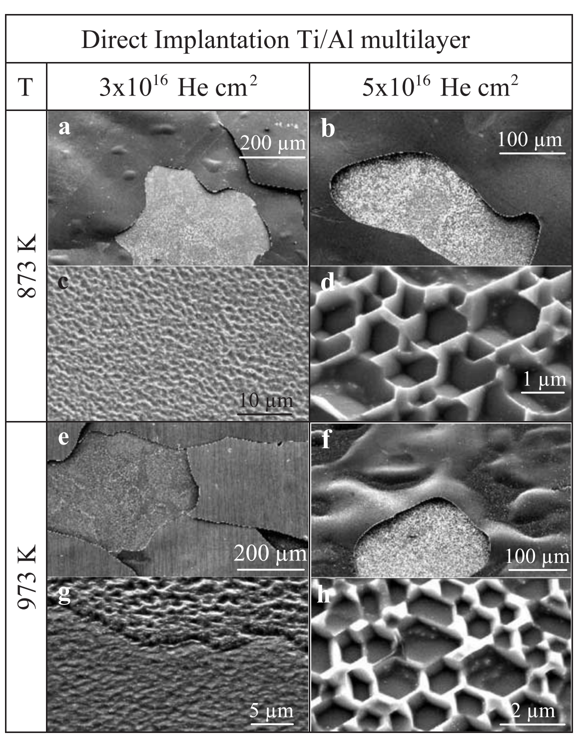

Fig. 7. Selection of SEM pictures in the direct-implanted area of the surface of the Ti/Al multilayer deposited on polycrystalline copper surface after helium implantation after annealing.

the copper substrate, with the periodical pattern of the microsieve nearly completely being interrupted at some of the grain boundaries.

3.2. Helium implantation on coated polycrystalline Cu

3.2.1. Multilayer Ti/Al

In the SEM pictures of Fig. 5, blistering phenomena are observed for all annealing temperatures between 773 and 973 K. Already after 773 K annealing, the blisters are visible with a height of 280 nm for the high fluence (Fig. 5b) and 70 nm for the low fluence (Fig. 5a) as measured by CSOM. The periodical pattern of the microsieve was reproduced with a distance of 9 μm between the nearest neighbours and 13 μm ($9\sqrt{2}$) between the second-nearest neighbours (in the diagonal direction). The blisters developed without cracking. In the area directly implanted, i.e., uniformly without microsieve, no changes were observed. After increasing the annealing temperature up to 873 K (Fig. 5c and d), the blisters are better observed, as for both fluences, their height increased up to approximately 450 nm. An annealing at 973 K produced an enhancement of the previous observations (Fig. 5e and f). The blister height increased to 480 nm for both implantation fluences. At the highest fluence, there is

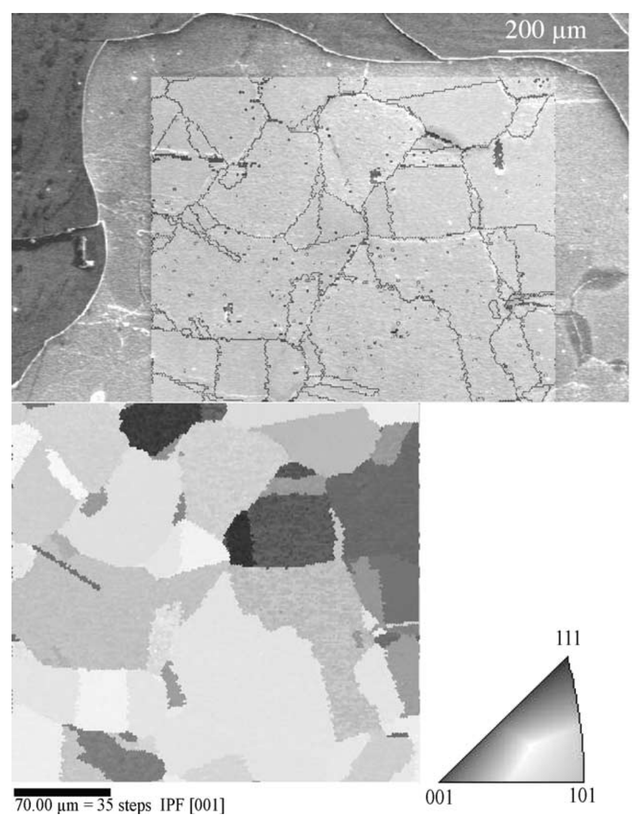

Fig. 8. Orientation Imaging Microscopy (OIM) experiments on the flaked surface of polycrystalline copper surface after helium implantation at 3×10^{16} He ions cm^{-2} and annealing at 973 K. In the upper figure, the grain boundaries obtained by OIM are superimposed on the SEM micrograph. In the bottom figure, a grey map indicates the orientation of each grain.

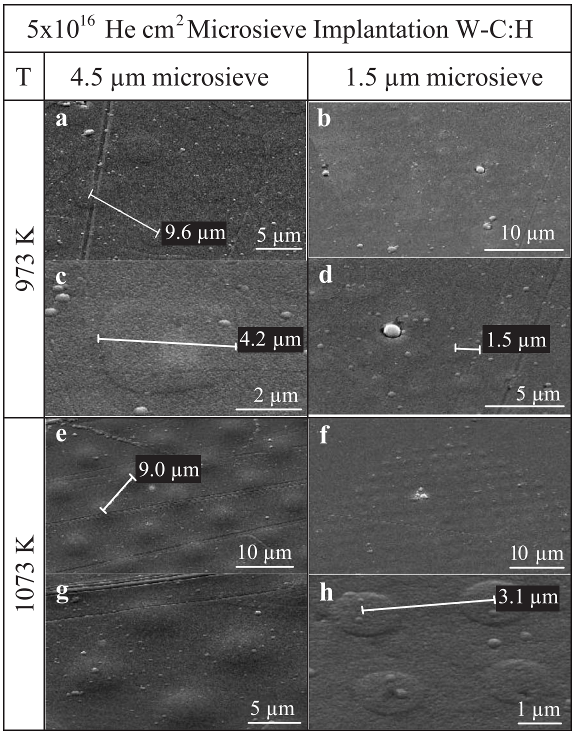

Fig. 9. Selection of SEM pictures in the microsieve area of the surface of W–C:H coating deposited on polycrystalline copper surface after helium implantation at 5×10^{16} He ions cm^{-2} through 1.5- and 4.5-µm microsieves and annealing.

some precipitation on the surface of the coating (Fig. 5f) which might be due to phase changes in the TiAl layer. In Fig. 6, height contours and profiles are shown for part of the blister area depicted in Fig. 5e. It can be noticed that the blisters extend further than the implantation area and that they are interconnected in the direction of nearest neighbours. This observation is related to delamination of the coating. An elevation of approximately 200 nm between adjacent blisters can be derived from the height profile recorded in that direction (see Fig. 6a). As observed for the lower annealing temperature, all the developed blisters did not show any cracking.

This is in contrast with observations for the direct-implanted areas. In Fig. 7, SEM pictures are shown in those areas. After annealing at 873 K, there is a massive blistering of the coating (elevations more than 30-µm high) observed with the naked eye and the occurrence of large flaking areas for both implantation fluences. In the flaked areas, the subsurface equilibrium bubbles have adopted crystallographic facets at the highest fluence (Fig. 7d and h), creating a cellular honeycomb structure with very thin walls in between the cells (r_{cell}=1 µm; wall thickness, ~50 nm). In the case of the low fluence, there was no development of the cellular structure, but a different surface porosity was observed depending on grain orientation (Fig. 7c and g). The coating after flaking still remains intact without any diffusion into the substrate and the protrusions seen in Fig. 5f for a non-delaminated layer. After annealing at 973 K, the flaking areas became more numerous. The dependence of the morphology of the cellular structure on the grain orientation was monitored by Orientation Imaging Microscopy (OIM) experiments as can be observed in Fig. 8.

3.2.2. W–C:H+Cr interlayer

In Fig. 9, the results of implantations through the microsieve masks are shown. Until 973 K, no signs of blisters were observed. At 973 K, blisters are hardly detected for the highest fluence at the 4.5-µm microsieve area (Fig. 9a and c) and even less clearly for the smaller pores size microsieve (Fig. 9b). The blisters are very flat (see, e.g., Fig. 9c), without showing interconnectivity between them. They have the same size as the microsieve holes. For the lowest fluence, the blisters were not observed (pictures not shown). An annealing higher at 1073 K allows observing the blisters more clearly. (Fig. 9e, f, g and h). At the 4.5-µm microsieve area, the blisters developed in a semispherical shape (Fig. 9g). In Fig. 10, height contours and height profiles are shown for a high fluence sample further annealed to 1073 K. The height of the blisters derived from Fig. 10a and b amounts to approximately 250 nm. On the other hand, at the 1.5-µm microsieve, the blisters

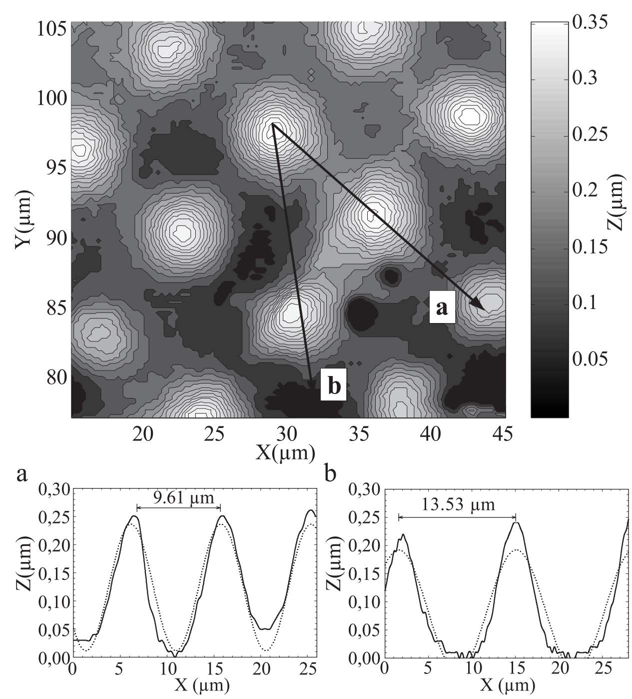

Fig. 10. Contour plot obtained from Scanning Confocal Scanning Optical Microscopy (CSOM) measurements performed on the surface of W–C:H coating deposited on polycrystalline copper surface after helium implantation at 5×10^{16} He ions cm^{-2} through a 4.5-µm microsieve after annealing at 973 K. The periodicity of the blistering pattern is clearly observed. The blisters are isolated both in the direction of the nearest neighbour (a) and in the diagonal direction (b). At the bottom of the figure, surface profiles in the (a) and (b) direction are shown.

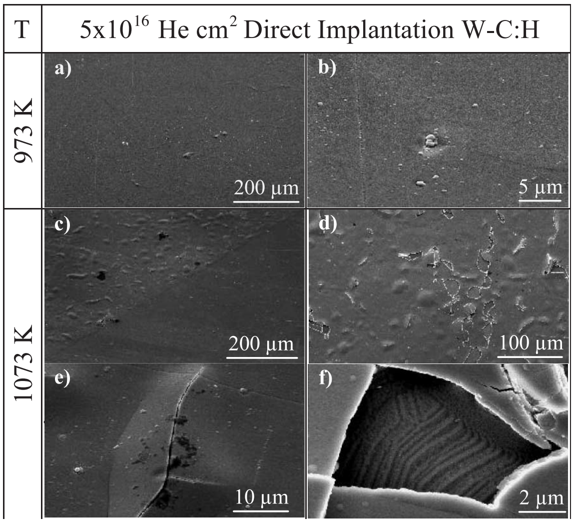

Fig. 11. Selection of SEM pictures in the direct-implanted area of the surface of W–C:H coating deposited on polycrystalline copper surface after helium implantation at 5×10^{16} He ions cm^{-2} and annealing.

appeared to remain very flat and shallow (45 nm high). In both cases, the blisters are isolated and they do not extend beyond the implanted area. No delamination was therefore detected.

Fig. 11 shows SEM pictures of the direct-implanted areas. After annealing to 973 K, some blistering is observed (Fig. 11a), but almost all the surface of the coating remains intact (Fig. 11b). Further annealing at 1073 K causes blistering (Fig. 11c and d) and flaking (Fig. 11f) of the coating. In Fig. 11e, it is observed that some of the blisters are cracked. Contrarily to the multilayer coating, no development of any cellular structure with crystallographic facets was observed in the flaked areas. A small-scale substructure was observed (Fig. 11f), probably related to the presence of the Cr adhesive interlayer.

3.3. Discussion

From the observations, it can be concluded that the implanted gas is released from the polycrystalline copper substrate at T>773 K and that it is collected at the interface. The bubbles are confined by the presence of the coating and developed into equilibrium bubbles with equilibrium pressure $P\sim2\,\gamma/R$, with γ as the surface energy and R as the radius of the bubble. In the case of the multilayer Ti/Al coatings, this leads to the formation of facetted structures in the substrate implanted with the highest fluence of 5×10^{16} ions/cm^2. Preferential low index facets occur because they have the lowest surface energy. For the lowest fluence (3×10^{16} ions/cm^2), no faceting is observed, but each copper grain develops a different surface porosity. This faceting and surface porosity causes dewetting and final flaking of the coating after annealing at T>873 K. When the implantation is performed through the 4.5-µm microsieve, the blisters observed after 873 K annealing are related to delamination of the film. For example, at 973 K, the pressure in the observed equilibrium bubbles (r_{cell}=1 µm) can be calculated to be approximately 60 bar. This pressure corresponds to a He concentration (c_{He}) of 1.8×10^{21} cm^{-3}. If we defined the average swelling caused by the helium as the ratio between the implanted fluence and c_{He}, we can estimate a swelling of 0.16 µm in the case of the sample pre-implanted with 3×10^{16} He ions/cm^2. After the formation of the blister (blister height H=0.45 µm), the pressure is reduced to 25 bar. Therefore, following Williams' approach (Eq. (1)), an energy release rate G can be estimated of approximately 0.5 J m^{-2}. This value is typical for interface energies of metal systems. It is interesting to note that the pressure causing the delamination of the film does not induce cracking of the 3-µm blisters. This is due to the fact that this critical pressure is inversely proportional to the square of the radius of the blister [7]. Therefore, the use of small blister radius as proposed in our test is more convenient. On the other hand, for the W–C:H coatings, blistering is not observed until annealing temperatures higher than 973 K are reached. The blistering does not induce any delamination of the film and the effect can be related to helium blistering only.

4. Conclusions and final remarks

The principle of a modified blister test based on gas pre-implantation in selected areas of the substrate has been proven to be successful when applied to the adhesion study of thin films. The localised gas implantation prior to coating deposition and subsequent annealing developed a periodical array of blisters in the coating surface. The size of the blisters indicated the occurrence of delamination. In the case of Ti/Al multilayers, annealing at 873 K causes delamination of the coating. No delamination and thus strong adhesion was found for W–C:H coatings (with an intermediate Cr adhesive) layer. In the latter case, the observed blistering is related only to helium swelling and blister formation corresponding to the implanted area. New morphologies of gas bubbles were observed in the copper substrates when they are confined by the surface coating. In uniformly implanted areas, different types of blisters, varying in size, shape and degree of deformation, provide additional information about the mechanical and adhesive properties of the thin film.

A foreseen drawback of the presently proposed test, which employs helium, is the high annealing temperature needed to promote the helium gas to the interface. Lowering of the maximum annealing temperature could be achieved introducing nitrogen or hydrogen with plasma or electrochemical treatments. An extension of the test would include the local heating of the coated and implanted samples by laser irradiation through a mask or microsieve. In the future, a Focused Ion Beam (FIB) facility will be used in order to obtain cross-sectional images through the blisters. Then, the delaminated area can be studied in detail.

Acknowledgements

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References

[1] H. Dannenberg, J. Appl. Polym. Sci. (1961) 125.
[2] M.L. Williams, J. Appl. Polym. Sci. 13 (1969) 29.
[3] J. Napolitano, A. Chudnovsky, A. Moet, J. Adhes. Sci. Technol. 2 (1988) 311.
[4] Y.H. Lai, D.A. Dillard, J. Adhes. Sci. 31 (1990) 177.
[5] Y.H. Lai, D.A. Dillard, J. Adhes. Sci. Technol. 8 (1994) 663.
[6] Yu.N. Borisenko, V.Y. Gritsyna, T.V. Ivko, J. Adhes. Sci. Technol. 9 (1995) 1413.
[7] J.G. Williams, Int. J. Fract. 87 (1997) 265.
[8] J.P. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids TRIM, Pergamon, New York, 1985.
[9] C. Strondl, G.J. van der Kolk, T. Hurkmans, W. Fleischer, T. Trinh, N.M. Carvalho, J.Th.M. de Hosson, Surf. Coat. Technol. 142 (2001) 707.
[10] C. Strondl, N.M. Carvalho, J.Th.M. de Hosson, G.J. van der Kolk, Surf. Coat. Technol. 162 (2003) 288.
[11] B.J. Kooi, R.J. Poppen, N.J.M. Carvalho, J.Th.M. de Hosson, M.W. Barsoum, Acta Mater. 51 (10) (2003) 2859.
[12] R. Escobar Galindo, A. van Veen, J.H. Evans, H. Schut, J.Th.M. De Hosson, Nucl. Instrum. Methods. Phys. Res., B 217 (2) (2004) 262.
[13] J.H. Evans, R. Escobar Galindo, A. van Veen, Nucl. Instrum. Methods. Phys. Res., B 217 (2) (2004) 276.